

SURFACE CHARACTERIZATION OF TITANIUM A TITANIUM ALLOYS PART III: EFFECT ON TI (c.p.) AND TI-8Mn OF LABORATORY CHEMICAL TREATMENTS SURFACE CHARACTERIZATION OF TITANIUM AND LABORATORY CHEMICAL TREATMENTS

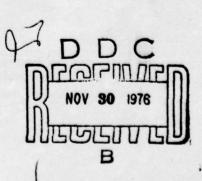
MECHANICS AND SURFACE INTERACTIONS BRANCH NONMETALLIC MATERIALS DIVISION

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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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20. Abetract (Continue on reverse side if necessary and identify by block number) This investigation is part three of a program which looks at the effects of surface treatments on surface chemistry and morphology of titanium and titanium alloys. This part discusses the effects of six laboratory surface treatments on titanium, commercially pure, and Ti-8Mn alloy.

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FOREWORD

This technical report was prepared by W. L. Baun and N. T. McDevitt, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio, and James S. Solomon, University of Dayton Research Institute, Dayton, Ohio. This work was initiated under Project 7340, "Nonmetallic and Composite Materials," and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Work unit monitor is Dr. William Jones.

This report covers work conducted inhouse during the period July 1975 through June 1976.

The authors wish to acknowledge the work of Victor Meyers of the University of Dayton and of Gary Fugate and William Lampert, student trainees.

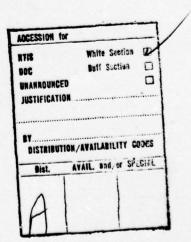


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SECTION I INTRODUCTION

The need for lighter, higher strength structures makes it necessary to develop new classes of materials such as composite and adhesively bonded materials. The surface composition and morphology of these metals, compounds and alloys are extremely important in their fabrication and use. The surface composition of many alloys bears little resemblance to the bulk composition. Segregation during heat treatment can result in surface properties (either deleterious or beneficial) far different from the bulk. Chemical treatments can selectively dissolve some components and not others, which results in large changes in composition and properties. Chemical treatments also can leave behind impurities both as combined and adsorbed species. McDevitt and coworkers have shown such phenomena for several aluminum alloys which were subjected to numerous chemical treatments (Ref. 1, 2). These aluminum alloys have been used extensively with adhesive bonding for secondary structures and are projected for use as primary load bearing members. Unfortunately, aluminum alloys, primarily because of low melting points, do not possess the properties necessary for advanced aerospace structures. Therefore, titanium and its alloys because of lightweight, thermal stability and high strength have been under development for aerospace applications. Conventional methods of joining titanium alloys such as welding, bolting and riveting are used, but just as in aluminum alloys, the advantages of adhesive bonding make it necessary to develop surface treatments for Ti which produce adhesive joints which are strong and durable. Adhesive joints possess a more uniform stress distribution, are lighter, and are better sealed against corrosion than conventional joints.

The requirement of operation in excess of 250°F places a severe burden on both the adhesive and the interfacial region between the adhesive and adherend in the joint. Joint failures under adverse conditions have often been blamed on the adhesive but a recent study (Ref. 3) suggests that the adherend surface may likely be the cause of failure in many cases. Surface treatments have been developed to give optimum bonding surfaces which produce durable bonded joints. This involves not only creating a surface of the proper structure and roughness, but also of the correct chemistry to ensure long time use under adverse conditions. It is therefore necessary to be able to determine elemental composition and morphology for a surface following each surface treatment. Certain treatments may be used to strip off the natural oxide in preparation for a treatment such as anodization, where the natural oxide is replaced by the anodic oxide of carefully controlled thickness. Other treatments etch the surface to provide mechanical (hook and latch) attachment of adhesive to adherend. Still others replace the natural oxide with a chemically formed oxide or conversion coating which is both bondable and durable.

In addition, many surface treatments and conditions are applied to titanium and its alloys for purposes other than adhesive bonding. For example, surface hardening is used to improve wear and galling resistance. Also, surfaces can be altered to produce improved appearance, to increase stress-corrosion resistance, or to improve fatigue properties. These alterations may be produced by gaseous diffusion, anodizing, metallic alloying, electroplating, flame spraying, hot dipping, and other coating methods. Alternatively, uncoated surfaces may be altered mechanically by such processes as peening, tumbling, or rolling, or by the finishing techniques of machining, grinding or chemical milling (Ref. 4).

In this work, we are investigating the effects on the surface of several surface treatments on Ti (commercially pure), Ti-6Al-4V, and Ti-8Mn. We are also looking at various structural aspects of titanium

oxides formed on the above materials. Finally, we are determining effects of some surface treatments on multiphase titanium alloys containing four or more elements. In Part I of this report we showed results of commercial treatments on Ti-6Al-4V (Ref. 5) and in Part II we showed surface effects on this same commercial alloy due to six laboratory treatments (Ref. 6). In this part of the report we show the effects of these same six laboratory treatments on Ti-8Mn and titanium (c.p.).

SECTION II EXPERIMENTAL

1. EQUIPMENT

a. ISS/SIMS

The primary characterization instrument used was ion scattering spectroscopy and secondary ion mass spectroscopy (ISS/SIMS). This dual method uses a low energy ion beam (1-3 KeV) to probe the surface. The ISS (ion scattering spectrometry) method (3M Company, St. Paul, Minnesota) measures the energy loss when the probing ion scatters from the outermost atom layer at the surface. The SIMS (secondary ion mass spectrometry) technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Advantages and operating parameters were outlined in Part I (Ref. 5) and the experimental setup was shown in both earlier reports (Refs. 5, 6). Appendices of mass and scattering information appear in this part of the report and were also included in Parts I and II (Refs. 5, 6) to aid the reader in spectral interpretation.

b. AES

Auger electron spectroscopy (AES) is based on the process of radiationless de-excitation of an excited atom by emission of electrons. This mechanism is often more probable than the radiative de-excitation by emission of an x-ray. For the matrix and alloying elements of concern in this work, the Auger electron yield per K electron vacancy is much higher than for the other mechanism of de-excitation, x-ray emission. The instrument used and described in Part II (Ref. 6) is the Model 540 thin film analyzer (Physical Electronics, Inc., Eden Prairie, Minnesota).

c. SEM

The scanning electron microscope (SEM) used in this work was the Quikscan (Coates and Welter Corp., Sunnyvale, California).

2. SURFACE CHEMICAL TREATMENTS

There are a large number of commercial surface chemical treatments available for titanium and titanium alloys. Five multistep commercial treatments were described in Part I (Ref. 5). Since most of these chemical solutions have proprietary formulations, the chemical solutions used in this study were relatively simple and were prepared in our laboratory. The solutions described in Table I represent a cross section of the chemistry found in most commercially prepared solutions. All chemicals used were of reagent grade quality.

TABLE 1
Surface Chemical Treatments for Titanium
And Titanium Alloys

Code	Description	Treatment
1	Degrease	Sample slurried in acetone, wiped dry, then ultrasonically cleaned in carbon tetrachloride for 5 minutes.
2	Alkaline	Sample submerged in 0.1N sodium hydroxide, room temperature for 2 minutes. Running tap H ₂ O for 15 minutes, standing deionized H ₂ O for 5 minutes.
3	HNO ₃ /HF	Sample submerged in a solution of 170ml nitric acid, 30ml hydrofluoric acid, 800ml distilled water, room temperature for 2 minutes. Rinse as in #2.
4	Na ₃ PO ₄ /NaF/HF	Sample submerged in a solution of 50g sodium orthophosphate, 9g sodium fluoride, 26ml hydrofluoric acid, distilled water to 1 liter, room temperature for 2 minutes. Rinse as in #2.
5	NH ₄ HF ₂	Sample submerged in solution of ammonium bifluoride (10g/liter) room temperature for 2 minutes. Rinse as in #2.
6	H ₂ SO ₄ /CrO ₃	Sample submerged in solution of 140g sulfuric acid, 14g chromium acid, distilled water to 1 liter, room temperature for 2 minutes. Rinse as in #2.

SECTION III RESULTS AND DISCUSSION

Parts I and II of this series of reports contain standard spectra and charts of ISS and SIMS data which aid the reader in interpretation of spectral data. In the interest of saving space some of this original reference data has been omitted and only Appendix A (Ion Scattering Peaks) and Appendix B (Isotopic Abundances) have been retained in this part of the report.

1. EFFECTS OF SURFACE TREATMENTS ON Ti, c.p.

Figure 1 shows scanning electron micrographs of commercially pure titanium subjected to each of the treatments outlined in Table 1. The number under each micrograph refers to the treatment number shown in the table. The surface topographic features do not change appreciably with treatment except with number four which is markedly different from the others. As will be shown later, this surface also exhibits surface chemical differences compared to the other samples.

Figures 2 through 13 show ISS, + SIMS and AES data for commercial titanium subjected to each surface treatment. As can be seen from Figures 2 and 3 (from degreased samples) the commercial titanium has numerous impurities, notably chromium, which is a bulk impurity but of higher concentration at the surface. Appendices C and D show the Auger electron spectra from an equilibrium sputtered surface, "ESS", for Ti, c.p. and Ti-8Mn respectively, for comparison with the data from treated surfaces. The equilibrium sputtered surface represents a surface sputtered with an inert ion beam until all spectral changes cease. It is recognized that this is an artificial surface state, but it is one which can be reproduced for reference purposes from laboratory to laboratory.

The ISS spectra shown in the figures are very sensitive to changes in oxygen/titanium stoichiometry and indicate except for treatment four that

the surface is covered with a TiO₂ coating. Often little information on alloying and impurity elements is given in ISS spectra because most of the elements of interest are obscured in the tails of titanium and oxygen. In addition titanium is one of the elements which exhibits severe low energy tailing due to unexplained non-binary scattering events. Because of these limitations for some materials, SIMS is an ideal complementary tool for use with ISS. In addition to separating each of the impurity and alloying elements, certain "fingerprint" spectral features give some information about chemical combination. Also, the ability to distinguish isotopes by the method allows doping the surface with enriched species.

Figures 4 and 5, spectra from alkaline washed specimens, show that many of the surface impurities have been removed. The surprisingly large carbon peak seen in the AES data cannot be explained except by contamination during or following surface treatments. The AES data represents spectra from the surface before any sputtering took place. The ubiquitous nature of carbon and the extremely high sensitivity of AES for that element account for its appearance in all spectra shown here.

Figures 6 and 7, spectra from HNO₃/HF acid etched samples illustrate the usefulness of using complementary surface spectroscopies rather than relying on only one method. The SIMS data shows, for instance, the presence of fluorine on the surface, while the AES data shows no indication of fluorine. SIMS spectra in the AES chamber taken before the electron beam is turned on also show fluorine. As soon as the electron beam is energized the mass 19 peak representing fluorine drops rapidly. RGA (residual gas analysis) spectra show a rapid increase of fluorine in the gas state when the electron beam is turned on. The high yield in + SIMS of F cannot be adequately explained since one would expect fluorine to prefer to be negatively ionized. The appearance of electron desorption of fluorine occurs only with certain treatments. Certain other treatments leave fluorine on the surface, the fluorine is not desorbed, and fluorine

appears in the Auger spectrum. Such phenomena probably indicate that fluorine exists in different samples in different chemically combined or uncombined states. Since this etch is used as a part of a number of treatments to expose fresh alloy for further treatment, it is important to know the surface chemical state following this etch. AES profiles, which are obtained by measuring AES peak heights as the surface is sputtered away, show oxide thickness to be slightly less than the natural oxide formed during processing as will be shown later.

Figures 8 and 9, spectra from Ti, c.p. exposed to treatment 4, exhibit characteristics completely unlike spectra from all other surface treated specimens. Figure 1 shows that the surface morphology of this surface is also unique. This treatment is similar to the phosphate-fluoride commercial treatment which reportedly forms a homogeneous oxide of the anatase structure, a metastable phase which has a slightly simpler more random structure. As we suggested in Part II (Ref. 6), perhaps the anatase structure is stabilized by impurity ions. Destabilization and reversion to the rutile structure could occur with outside stimuli such as heat or under operating conditions of heat and humidity. Such a reversion is accompanied by a change in cell volume of about eight percent which presumably would be destructive to good adhesive bonding. An important feature seen in the spectra of specimens treated by No. 4 is the presence of fluorine in ISS, SIMS and AES data. The stability of fluorine in this specimen compared to the instability seen in the samples treated by No. 3, adds further credence to the idea of fluorine occurring in more than one chemical state in the coatings formed on titanium by chemical treatments.

Figures 10 and 11 show spectra from specimens subjected to treatment No. 5, NH₄HF₂. The ammonium bifluoride treatment provides a reactive solution to titanium in the pH 5 region, creating an oxide film similar to several other treatments. Ammonium bifluoride on the other hand, produces an unusual surface on aluminum alloys and will be discussed later.

Figures 12 and 13 depict spectra obtained from specimens treated by the acidic solution containing $\rm H_2SO_4$ and $\rm CrO_3$.

Special care must be taken to ensure that solutions do not contain impurity ions, particularly copper, which will deposit on the surface during etching. Figure 14 shows scanning electron micrographs of a sample etched by fresh HNO₃/HF solution in 3a, and by HNO₃/HF solution previously used for 2024 aluminum alloy in 3b. The light colored material virtually obscuring the surface in 3b is primarily copper as shown by the ISS data seen in Fig. 15. The effect on both surface chemistry and surface morphology seems to depend only on the copper present and not on other ions. Figure 16 shows ISS data for Ti, c.p. treated with HNO₃/HF to which metallic copper was added (a) and to which 2024 aluminum was added (b). The spectra are virtually identical. The ISS data provide unmistakable identification of copper. Such unambiguous results may not be obtained using only SIMS as shown in Fig. 17. Here the Cu isotopes (63 and 65) occur at the same nominal mass as ⁴⁷Ti ¹⁶O ⁺ and ⁴⁹Ti ¹⁶O ⁺. In addition, ⁴⁸Ti ¹⁶O ¹H ⁺ also appears at nominal mass 65.

None of the treatments described here which leave the surface covered with a simple oxide seems to build up a thick layer. Each is of the same order of magnitude as the oxide present on the as received material. Figures 18 and 19 show elemental profiles obtained using Auger electron spectra for the original degreased surface and one treated with HNO₃/HF. Both samples were sputtered with ⁴⁰Ar + under the same conditions. The vertical mark on the time axis represents the start of sputtering. The gradual build up of carbon before sputtering is begun, is probably real, resulting from migration of carbon from the bulk to the surface upon heating of the surface with the electron beam. Figure 20 is a similar profile for as received Ti-8Mn and shows an identical oxide thickness compared to Ti, c.p.

2. EFFECTS OF SURFACE TREATMENTS ON Ti-8Mn

Figure 21 shows scanning electron micrographs for specimens treated by each preparation described in Table 1. As can be seen, the surface morphology of 1, 2, 3, and 6 are similar and 4 and 5 are individualistic. All have a different appearance compared to the same treatments on Ti c.p. (Fig. 1) and Ti-6Al-4V (Ref. 6).

Figures 22 through 33 are ISS, SIMS, and AES data for Ti-8Mn subjected to the surface treatments outlined in Table 1. Spectra are shown for reference purposes for future work but separate results will not be discussed.

SECTION IV CONCLUSIONS

The combination of the four surface characterization methods used here allows changes in morphology (SEM) and elemental chemistry (ISS, SIMS, AES) to be effectively followed. From the elemental analysis standpoint, SIMS is especially sensitive to many of the elements commonly found in chemical treatments and complements both ISS and AES. This information will be useful for future reference in an experimental program on bondability and durability of titanium and titanium alloy surfaces.

REFERENCES

- 1. N.T. McDevitt, W.L. Baun, and J.S. Solomon, AFML-TR-75-122.
- 2. N.T. McDevitt, W.L. Baun, and J.S. Solomon, AFML-TR-76-13.
- 3. W.C. Hamilton and G.A. Lyerly, Picatinny Arsenal Report 4185, March 1971.
- 4. D.N. Williams and R.A. Wood, MCIC Report 71-01, "Effects of Surface Conditions on The Mechanical Properties of Titanium and Its Alloys", August 1971.
- 5. W.L. Baun, AFML-TR-76-29, Part I.
- 6. W.L. Baun, N.T. McDevitt, and J.S. Solomon, AFML-TR-76-29, Part II.

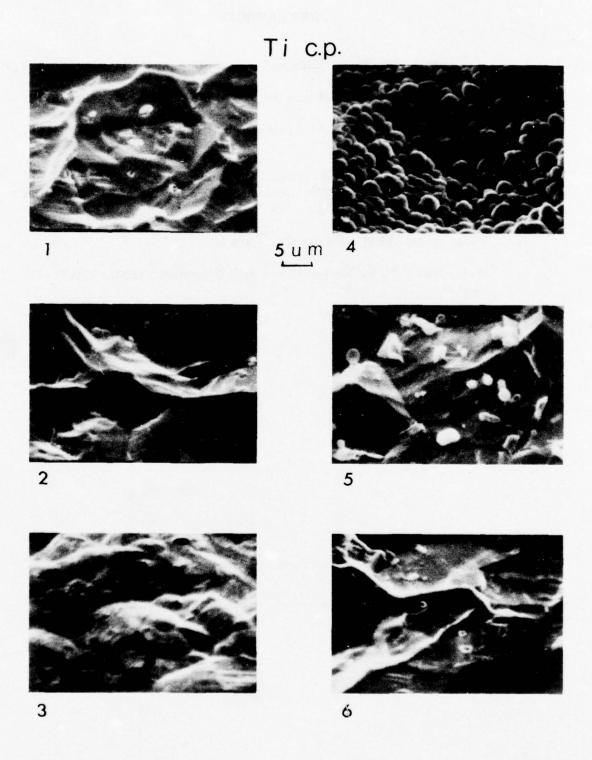


Figure 1. Scanning Electron Micrographs of Ti (c.p.)
Exposed to Treatments of Table I.

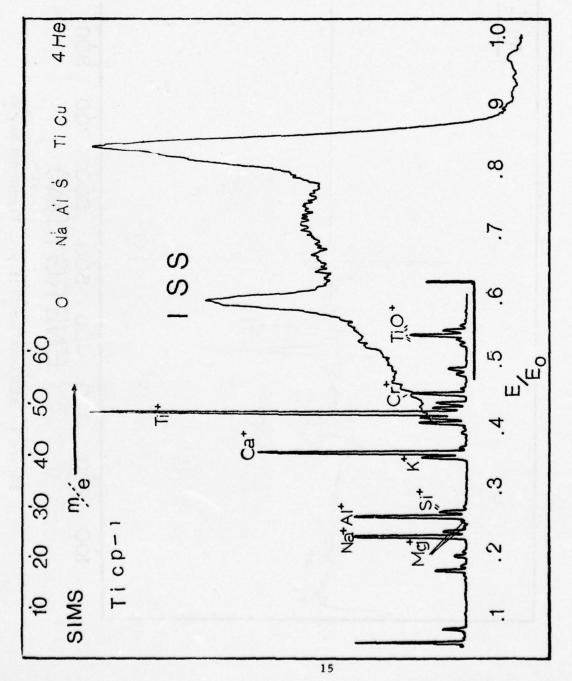


Figure 2. ISS/SIMS Data for Ti (c.p.), Treatment No. 1.

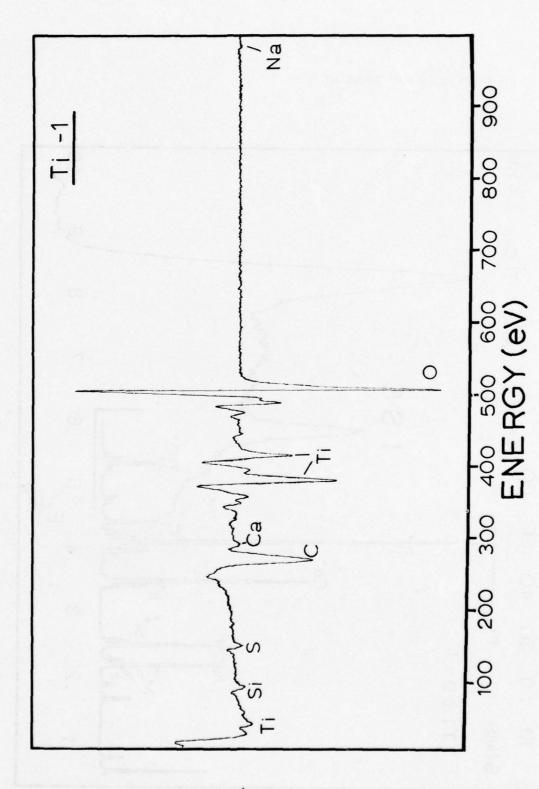


Figure 3. AES Data for Ti (c.p.), Treatment No. 1.

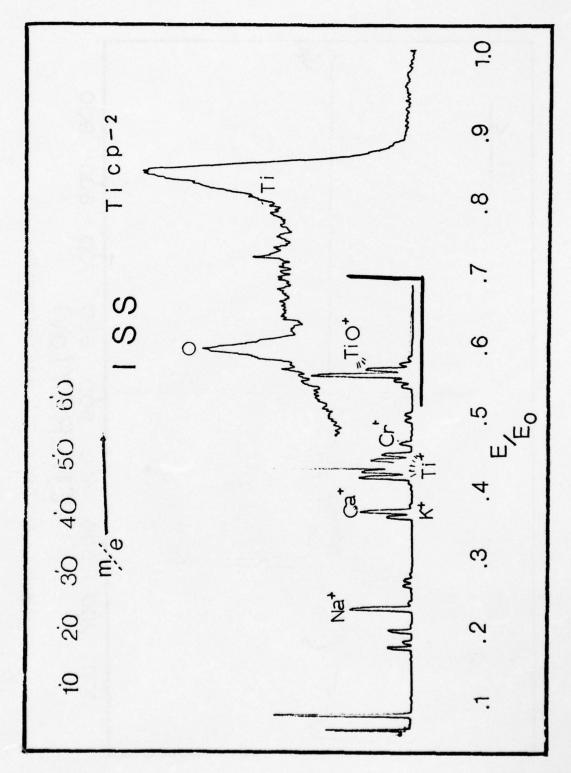
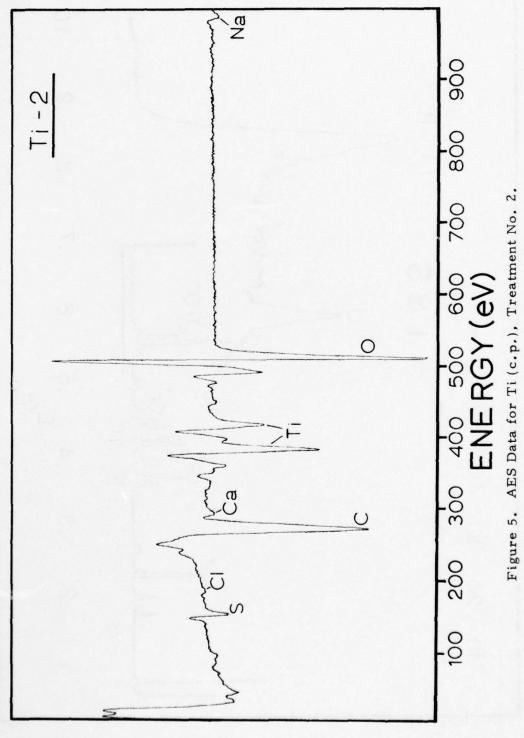


Figure 4. ISS/SIMS Data for Ti (c.p.), Treatment No. 2.



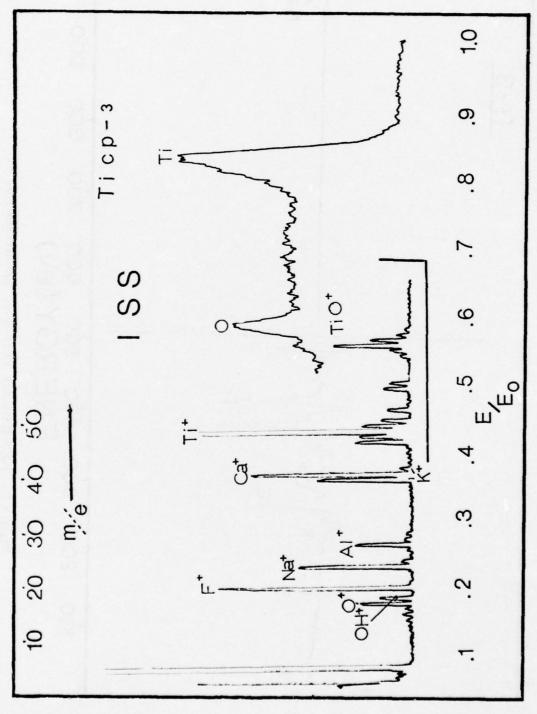


Figure 6. ISS/SIMS Data for Ti (c.p.), Treatment No. 3.

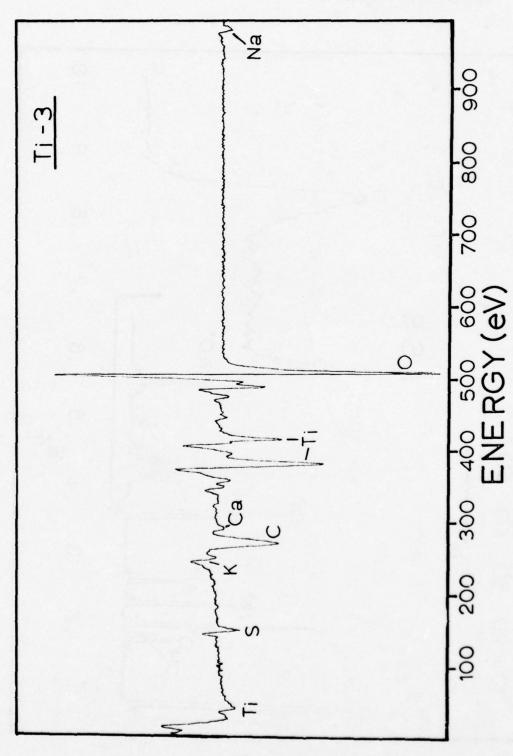


Figure 7. AES Data for Ti (c.p.), Treatment No. 3.

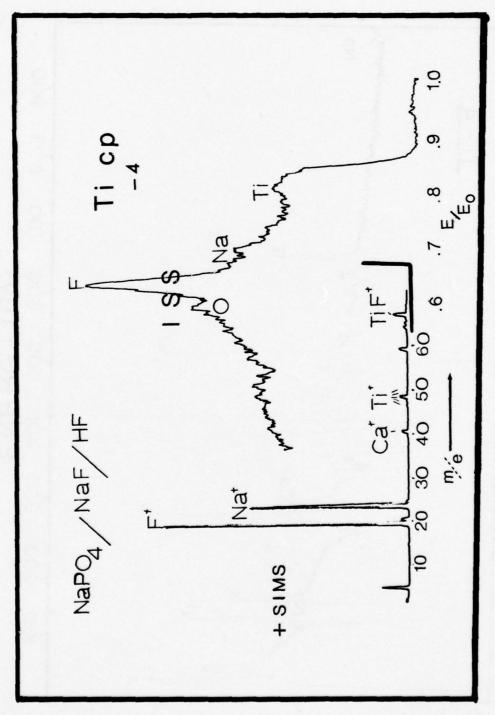


Figure 8. ISS/SIMS Data for Ti (c.p.), Treatment No. 4.

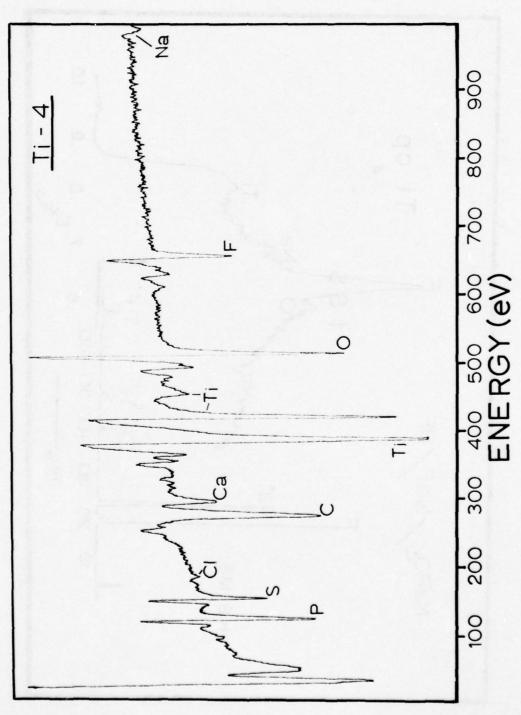
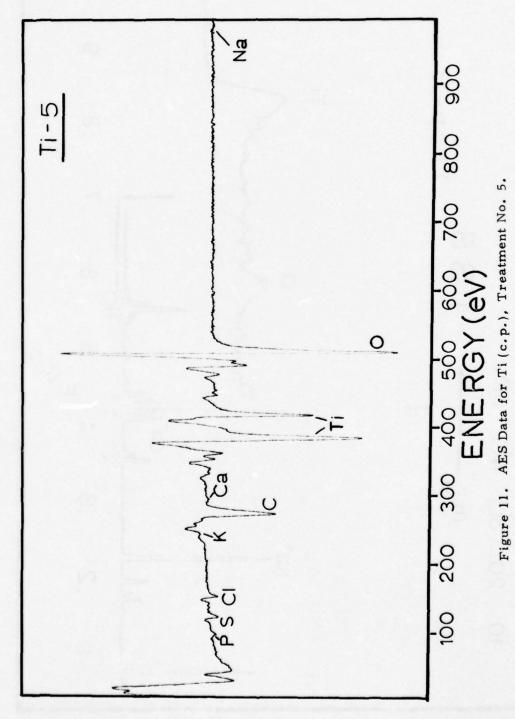


Figure 9. AES Data for Ti (c.p.), Treatment No. 4.

igure 10. ISS/SIMS Data for Ti (c.p.), Treatment No. 5.



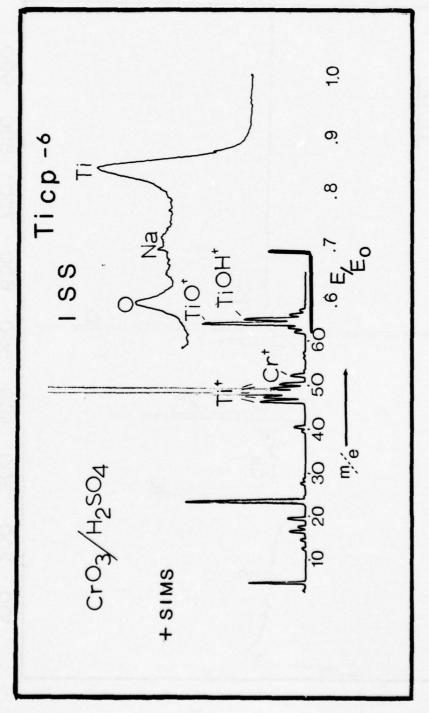


Figure 12. ISS/SIMS Data for Ti (c.p.), Treatment No. 6.

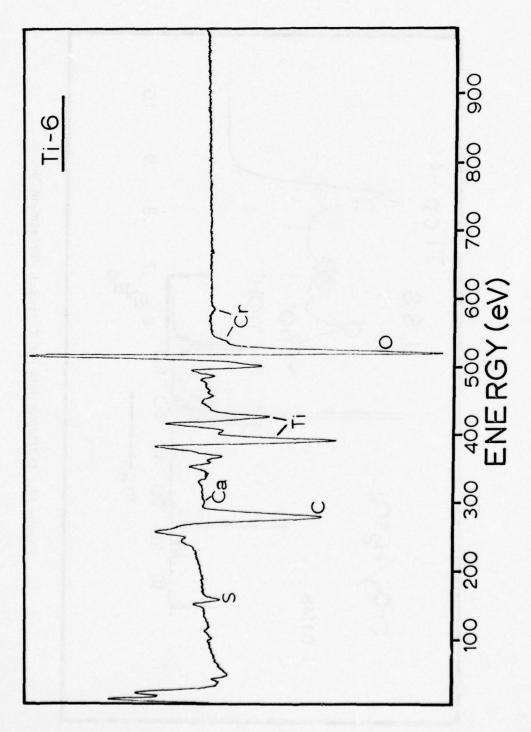


Figure 13. AES Data for Ti (c.p.), Treatment No. 6.

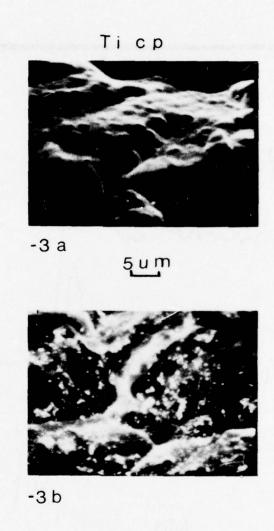


Figure 14. Scanning Electron Micrographs of
Ti, c.p. Treated with Fresh HNO₃/HF
(Treatment 3) 3A, and "Old" Solution
Previously used for 2024 Aluminum Alloy.

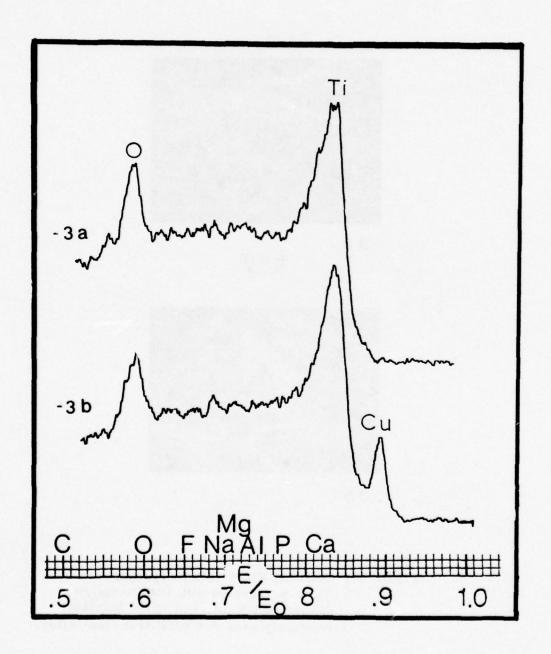


Figure 15. ISS Data for Specimens Described in Figure 14.

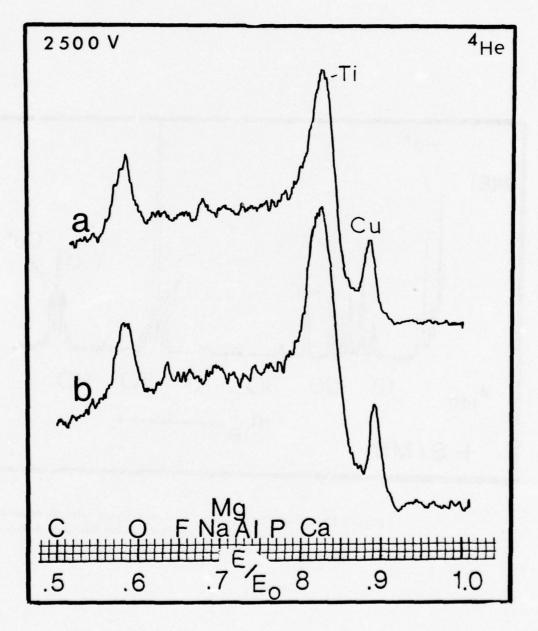


Figure 16. ISS Data for Ti, c.p. Treated with Treatment 3 to Which Has Been Added Metallic Copper (a) and 2024 Aluminum Alloy (b).

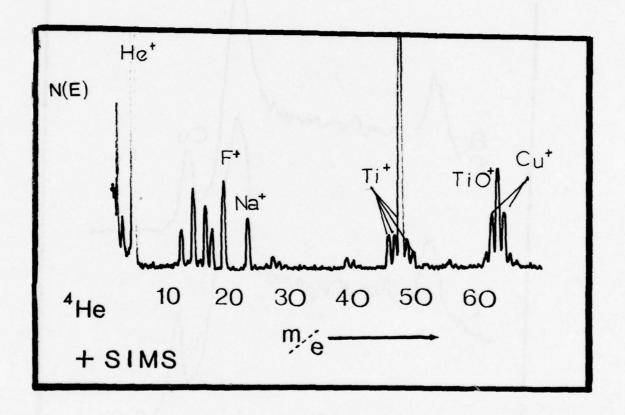
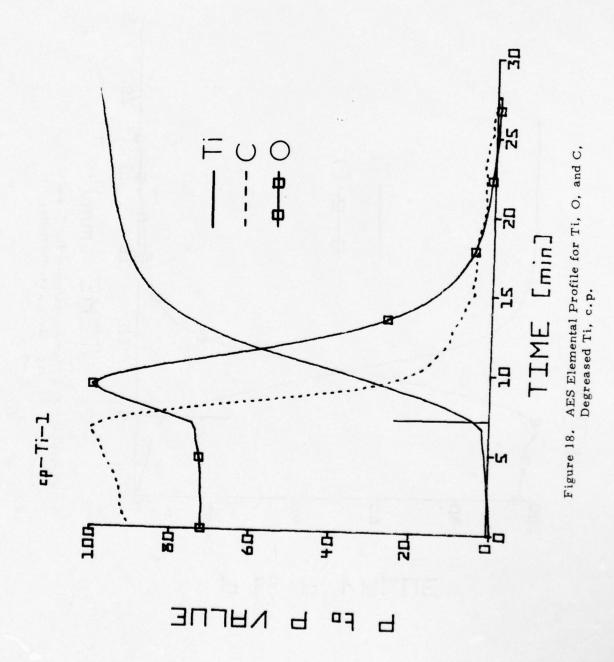
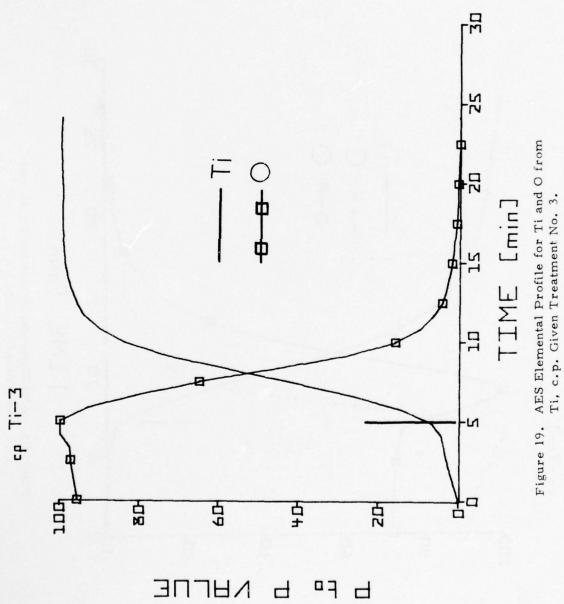


Figure 17. SIMS Data rom Ti, c.p. Treated with Treatment 3 to Which 2024 Aluminum Alloy Had Been Added.



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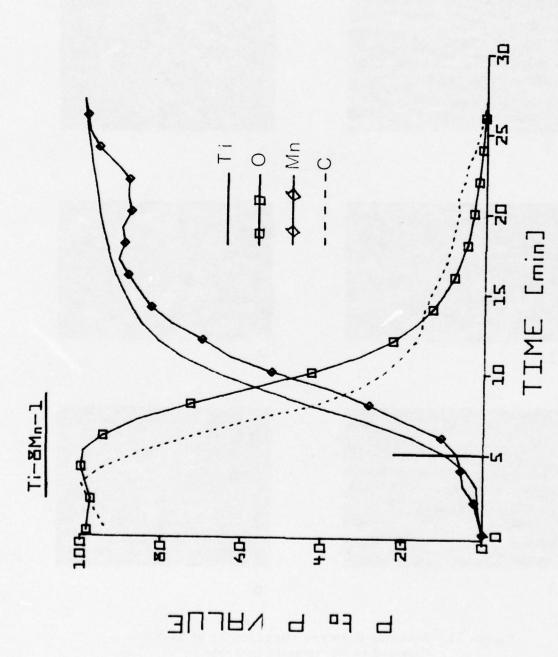


Figure 20. AES Elemental Profile for Ti, O, C, and Mn for Degreased Ti-8Mn Alloy.

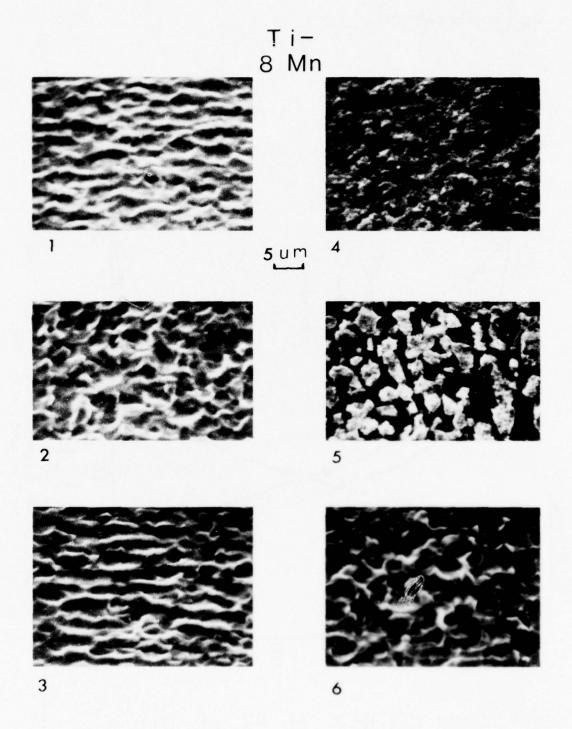


Figure 21. Scanning Electron Micrographs of Ti-8Mn Exposed to Treatments in Table 1.

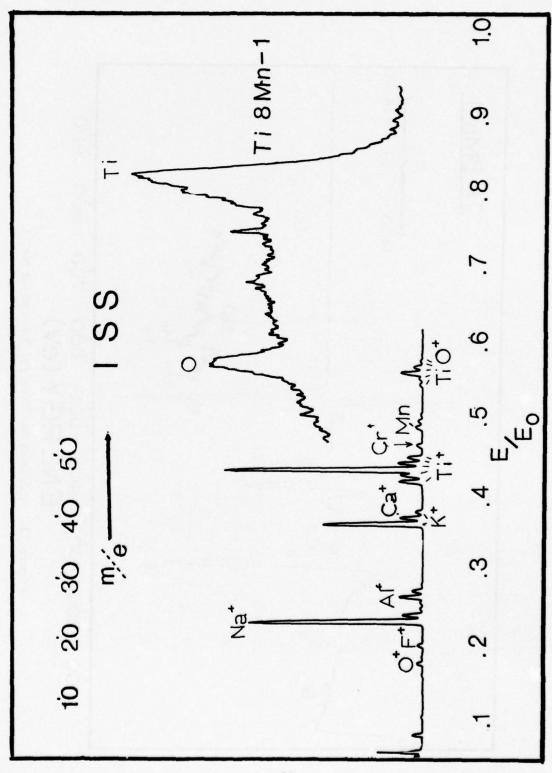
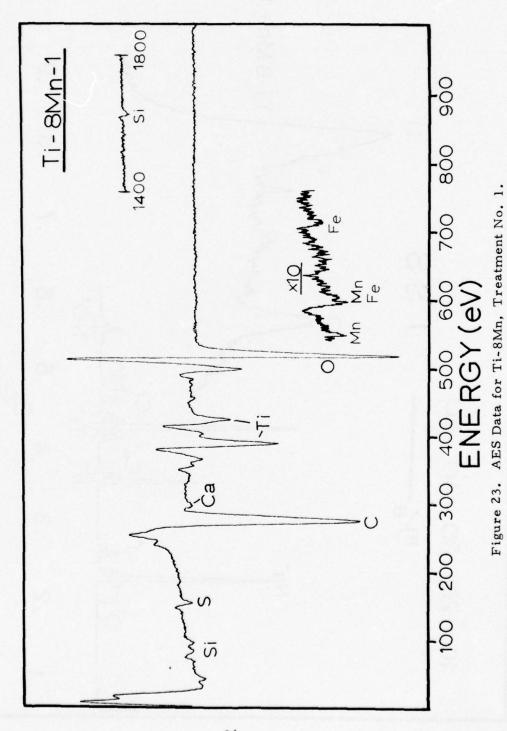


Figure 22. ISS/SIMS Data for Ti-8Mn, Treatment No. 1.



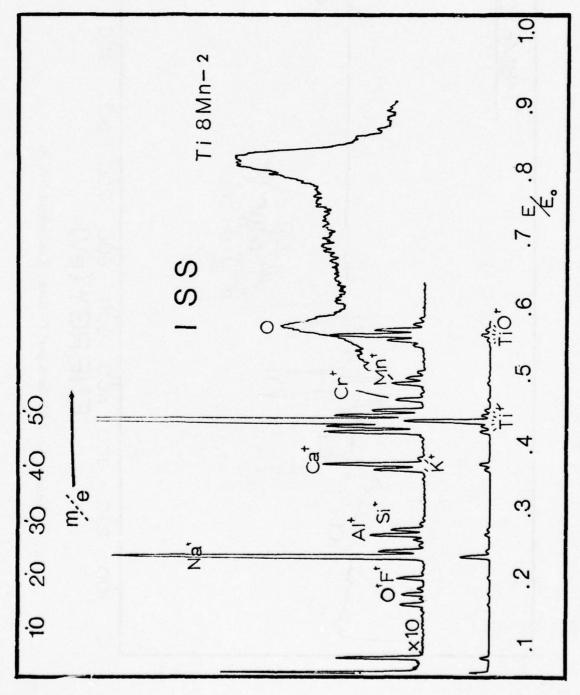


Figure 24. ISS/SIMS Data for Ti-8Mn, Treatment No. 2.

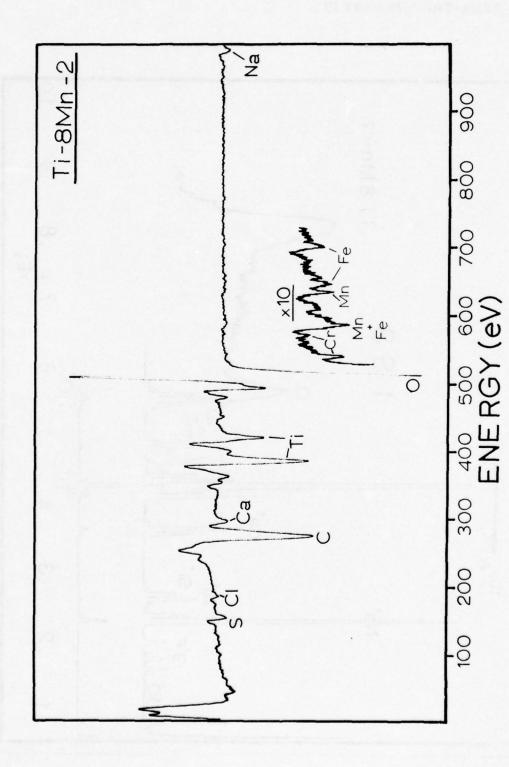


Figure 25. AES Data for Ti-8Mn, Treatment No. 2.

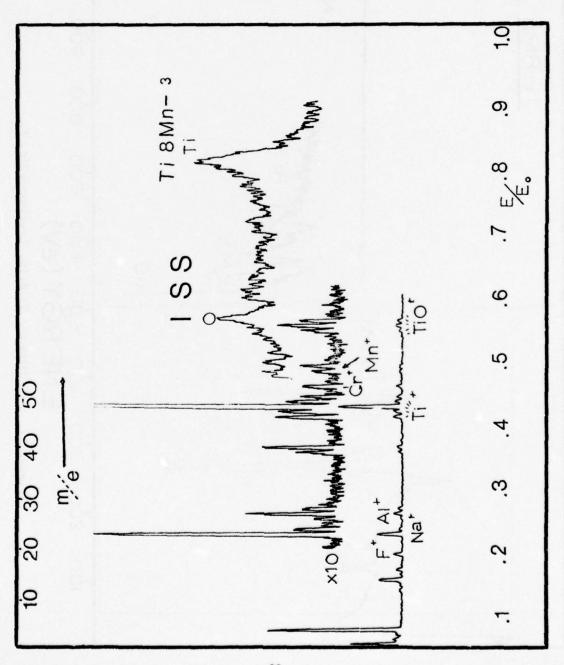


Figure 26. ISS/SIMS Data for Ti-8Mn, Treatment No. 3.

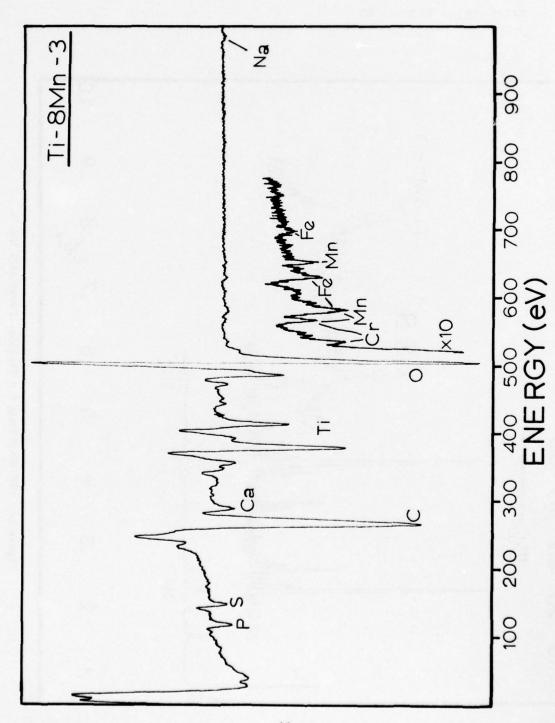


Figure 27. AES Data for Ti-8Mn, Treatment No. 3.

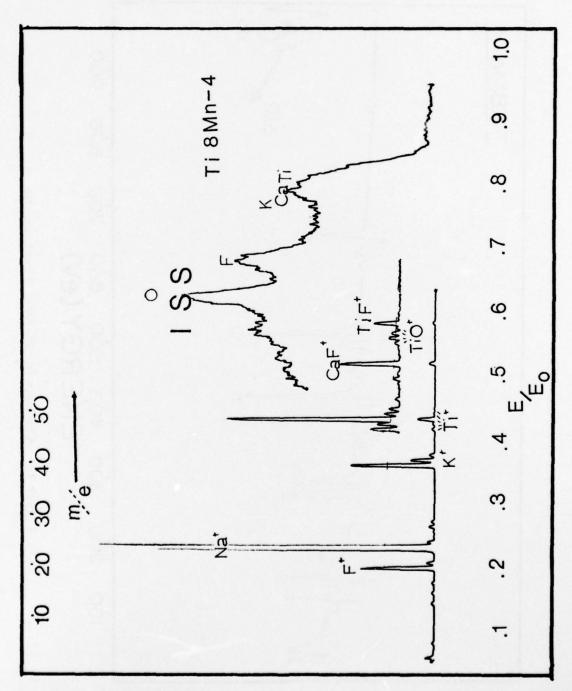


Figure 28. ISS/SIMS Data for Ti-8Mn, Treatment No. 4.

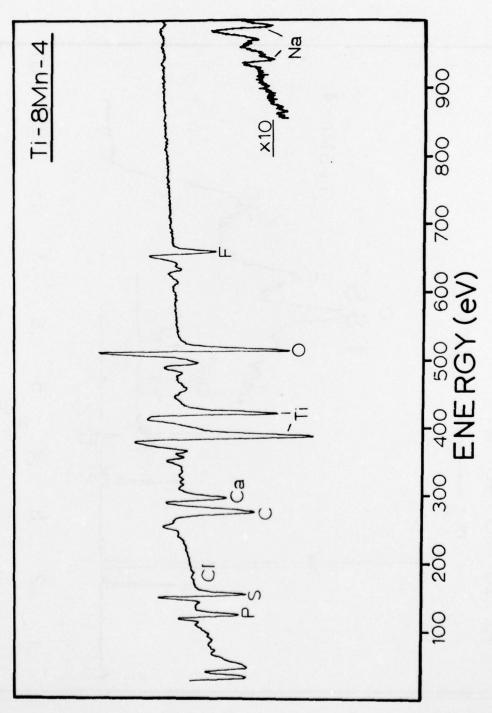


Figure 29. AES Data for Ti-8Mn, Treatment No. 4.

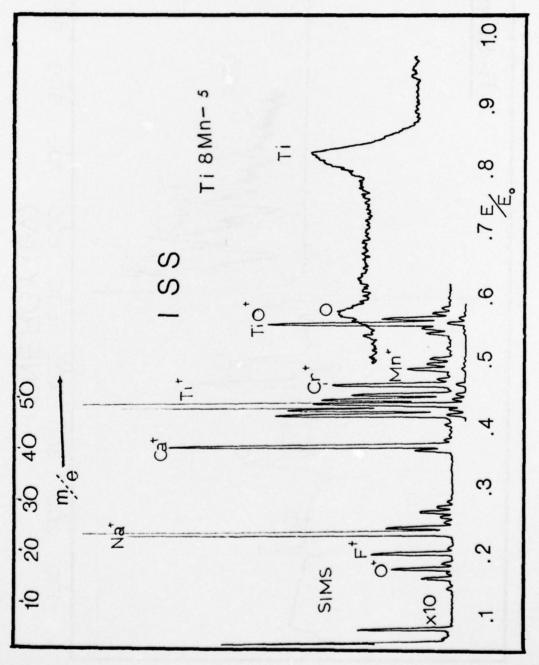


Figure 30. ISS/SIMS Data for Ti-8Mn, Treatment No. 5.

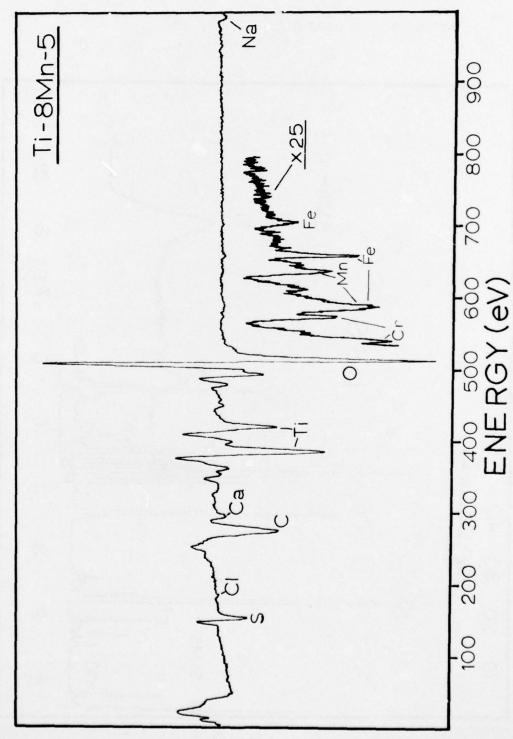


Figure 31. AES Data for Ti-8Mn, Treatment No. 5.

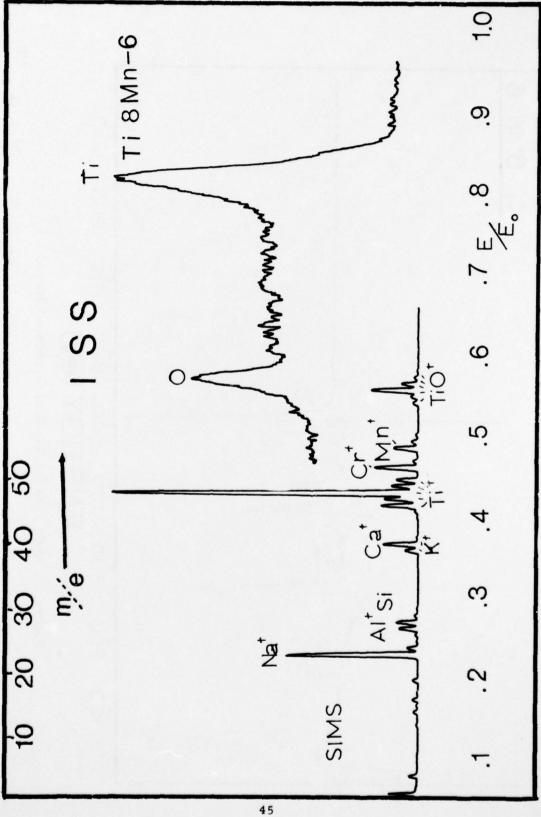
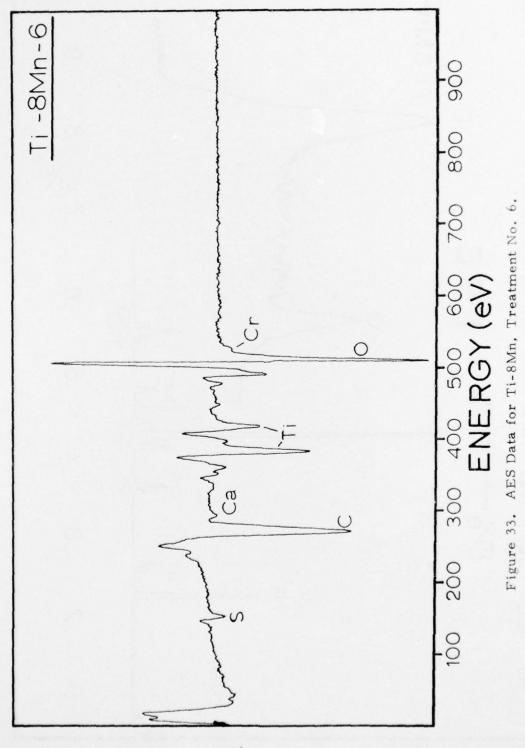


Figure 32. ISS/SIMS Data for Ti-8Mn, Treatment No. 6.



APPENDIX A

Ion Scattering Data (E/E $_{o}$ at 90°) for Z = 1 - 50

AFML-TR-76-29 PART III

E	LEMENT		1	E/E _O (at 0 = 90°)								
z	A		3 _{He}	4 _{He}	20 _{Ne}	40 _{Ar}						
1	1.0	Н										
2	4.0	He	.143	0								
3	6.9	Li	.393	.266								
4	9.0	Be	.500	.385								
5	10.8	В	.565	.459								
6	12.0	С	.600	.500								
7	14.0	N	.647	.555								
8	16.0	0	.684	.600								
9	19.0	F	.727	.652								
10	20.2	Ne	.741	.669	.005							
11	23.0	Na	.769	.704	.070							
12	24.3	Mg	.780	.717	.097							
13	27.0	A1	.800	.742	.149							
14	28.1	Si	.807	.751	.168							
15	31.0	P	.824	.771	.216							
16	32.1	S	.829	.778	.232							
17	35.5	C1	.844	.797	.279							
18	39.9	Ar	.860	.818	.332							
19	39.1	ĸ	.857	.814	.323							
20	40.1	Ca	.861	.819	.334	.001						
21	45.0	Sc	.875	.837	.385	.059						
22	47.9	Ti	.882	.846	.411	.090						
23	50.9	V	.889	.854	.436	.120						
24	52.0	Cr	.891	.857	.444	.130						
25	54.9	Mn	.896	.864	.466	.157						
26	55.8	Fe	.898	.866	.472	.165						
27	58.9	Co	.903	.873	.493	.191						
28	58.7	Ni	.903	.872	.492	.189						
29	63.5	Cu	.910	.881	.521	.227						
30	65.4	Zn	.912	.885	.532	.241						
31	69.7	Ga	.917	.891	.554	.271						
32	72.6	Ge	.921	.896	.568	.290						
33	74.9	As	.923	.899	.578	.304						
34	79.0	Se	.926	.904	.596	.328						
35	79.9	Br	.928	.905	.600	.333						
37	83.8 85.5	Kr	.931	.909	.615	.354						
38	85.5 87.6	Rb Sr	.932 .934	.911	.621 .628	.363 .373						
39		Sr Y		.913								
40	88.9 91.2	Zr	.935 .936	.914 .916	.633 .640	.379 .390						
41	92.9	Nb	.936	.917	.646	.398						
42	95.9	Mo	.939	.920	.655	.411						
43	99	Tc	.941	.922	.664	.424						
44	101.1	Ru	.942	.924	.670	.433						
45	102.9	Rh	.943	.925	.675	.440						
46	106.4	Pd	.945	.928	.684	.454						
47	107.9	Ag	.946	.929	.387	.459						
48	112.4	Cd	.948	.931	98	475						
49	114.8	In	.949	.933	.703	.483						
50	118.7	Sn	.951	.935	712	496						

APPENDIX B

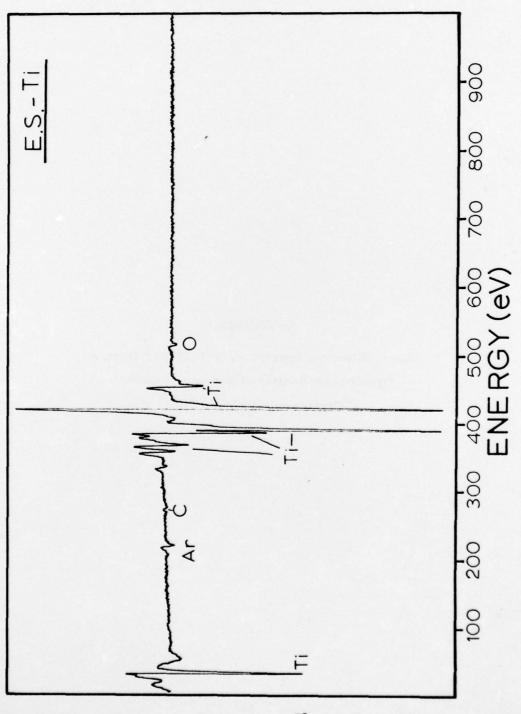
Relative Abundances of Naturally Occurring

Isotopes, Z = 1 - 44

•	A	1	2	3	4	5	6	7	8	g	10	11	12	13	14	15	16	17	18	19	20
1	H	99 9	01																		
2	He				100			00.0		-										1	
3	Li						7.4	92 6		100											
4	Be									100	183	017									
5	B										103	81.7	98 9	1.1							
7	N												30 3	1.1	99 6	04					
8	Ö														33 0	0.4	998	0.04	0.20		
9	F																350	004	020	100	
10	Ne																				90 9
71	A	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
10	(Ne)	03	88																		
11	Na	-	-	100																	
12	Mg	-	-	-	786	101	113														
13	AI				-			100													
14	Si					-			92 2	4.7	31										
15	P		-	-			-				-	100									
16	S					-	-	-	-				95 0	0.8	4.2		0 02				
17	CI														_	75.5		24 5			
18	Ar															_	0 34		0 06		99.6
19	K														_					93.1	0 01
20	Ca	1	42	42	44	AE	AC	47	40	40	EO	51	52	53	54	55	56	57	58	59	97 0
19	A-K	69	42	43	44	45	46	47	48	49	50	31	52	33	34	99	36	37	26	29	60
20	Ca	0.3	-06	01	21		003		02												
21	Sc		- 0 6	0.1		100	.003		U.Z												
22	Ti					100	80	73	74 0	5.5	5.2										
23	V						0.0	7.5	74.0	3.3	03	99 7									
24	-Cr										43	00,	838	96	23						
25	Mn															100					
26	Fe														-58		917	22	03		
27	Co																			100	
28	Ni	_																_	67 8		26 2
7+	A-	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
28	(Ni)	12	3.6		12																
29	Cu	-		691		30 9															
	Zn	-		-	48 9		27 8	41	186		0.6										
30						Commence.				60.5		395	- 1								
30 31	Ga	-	-				The state of the s			00.0											
30 31 32	Ge										20 5		27 4	7.7	36 7		7.7				
30 31 32 33	Ge As									-			27 4	7.7	-	100					
30 31 32 33 34	Ge As Se												27 4	7.7		100	9.0	7.6	23.5		49 8
30 31 32 33 34 35	Ge As Se Br												27 4	7.7	-	100		7.6		50 6	
30 31 32 33 34 35 36	Ge As Se Br Kr	81	82	83	84	85	28	87			20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 7	Ge As Se Br Kr	1	82	83	84	85	86	87	88	89		91	92	93	-	95		7.6 97		50 6	
30 31 32 33 34 35 36 7	Ge As Se Br Kr A- (Se)	49.4	92				86	87			20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 Z+ 34 35	Ge As Se Br Kr A- (Se) (Br)	49.4	92								20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 7	Ge As Se Br Kr A- (Se)	49.4	92	83	56 9		17.4		88		20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 7 34 35 36 37 38	Ge As Se Br Kr A- (Se) (Br) (Kr)	49.4	92		56 9		17.4	27 8	88		20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 7 34 35 36 37 38 39	Ge As Se Br Kr A+ (Se) (Br) (Kr) Rb Sr Y	49.4	92		56 9		17.4		88		20 5				09		90		0 4	50 6	23
30 31 32 33 34 35 36 7 34 35 36 37 38 39 40	Ge As Se Br Kr A+ (Se) (Br) (Kr) Rb Sr Y Zr	49.4	92		56 9		17.4	27 8	88	89	20 5		92		09		90		0 4	50 6	23
30 31 32 33 34 35 36 2, 34 35 36 37 38 39 40 41	Ge As Se Br Kr A+ (Se) (Br) (Kr) Rb Sr Y Zr Nb	49.4	92		56 9		17.4	27 8	88	89	90	91	92		94		90		0 4	50 6	23
30 31 32 33 34 35 36 7 34 35 36 37 38 39 40 41 42	Ge As Se Br Kr A- (Se) (Br) (Kr) Rb Sr Y Zr Nb Mo	49 4	- 92	11 5	56 9 - 0 6	722	17.4	27 8	88	89	90	91	92	93	94		90	97	0 4	50 6	23
30 31 32 33 34 35 36 2, 34 35 36 37 38 39 40 41	Ge As Se Br Kr A+ (Se) (Br) (Kr) Rb Sr Y Zr Nb	49 4	- 92		56 9 - 0 6	722	17.4	27 8	88	89	90	91	92	93	94	95	96	97	04	50 6	23

APPENDIX C

Auger Electron Spectrum, 0-1000 eV, from an Equilibrium Sputtered Surface, "ESS", of Commercially Pure Titanium



APPENDIX D Auger Electron Spectrum, 0-1000 eV, from an Equilibrium Sputtered Surface, "ESS", of Ti-8Mn

